Crystalline Transitions and Mechanical Resonance Dispersion in Vinyl and Ethyl Stearate*

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Dynamic shear compliance measurements on vinyl and ethyl stearate yield results depending critically on the particular crystalline modification in which these materials exist at the time of measurement. When first crystallized from the melt the materials are in a metastable state and only a few very small resonance dispersions are found in the range 50 to 5000 cps. At later times many large resonances occur; the largest is in the vicinity of 300 cps for both vinyl and ethyl stearate. While vinyl stearate is in its metastable state (about 60 days) a reversible transition takes place at $24.8_5 \pm 1_5 °C$ such that above this temperature there are no resonances from 50 to 600 cps, but below the transition point the large resonance near 300 cps always appears. A break in the slope of density-temperature curves for vinyl stearate occurs between 25 and 24°C indicating that a transition occurs in the vinyl stearate while in its β form (with the molecules tilted with respect to the planes formed by the terminal groups). X-ray powder diffraction photographs show no changes in the long spacing between planes so the transition must involve alterations in cross-sectional packing of the chains or a change from a monoclinic to triclinic unit cell rather than a variation in angle of tilt. While the details of the crystalline modification at 24–25°C are not as yet sufficiently clear to define a specific mechanism for the resonance phenomena, the results do prove conclusively that the dispersions are intimately connected with the crystalline state of the material. Eventually a kind of mechanical spectroscopy may be evolved yielding information on the actual crystalline state of solids in much the same way that electromagnetic spectra now aid in determinations of molecular structures.

I. INTRODUCTION

SHARP mechanical resonance dispersions in the audio-frequency range have been found in previous measurements of the dynamic shear compliance $(J^* = J' - iJ'')$ of polycrystalline metals,[1] crystalline polymers,[2,3] single crystals of quartz[4] and fused quartz,[4] and single crystals of sodium chloride, copper sulfate, and Rochelle Salt.[5] The resonances were found to be independent of sample dimensions,[2-4] but to depend on the static stress and thermal histories of the samples. Resonances observed in highly crystalline ($\sim 90\%$) polyvinyl stearate were much larger than those observed in other materials and this fact suggested that measurements on the monomer, vinyl stearate, would be of interest. The long side chains present in polyvinyl stearate must make a high degree of order in the polymer possible only if there is side chain crystallinity, i.e., it is difficult to conceive of the main polymer chains lining up in any regular fashion without a regular side chain structure. Hence the crystal structures of the polymer and monomer might be similar and the same type of mechanical behavior found.

Another consideration was that long chain hydrocarbon compounds such as vinyl and ethyl stearate are known to exist in a variety of crystalline modifications[6-11] so that changes in the mechanical resonance spectra could be expected to occur with changes in crystal form. A correlation between known changes in crystalline form and the resonances could then possibly lead to an explanation of these puzzling phenomena.

Measurements of the storage compliance J' and the loss compliance J'' made at closely spaced frequency intervals in the range 100 to 5000 cps and at temperatures and times corresponding to different crystalline forms are described. The results in part bear out the expectations previously cited.

II. MATERIALS STUDIED

The vinyl stearate and ethyl stearate used were furnished by the United States Department of Agriculture, Agricultural Research Service. The ethyl stearate contained less than 0.3% stearic acid and had a saponification value of 180.0 (theoretical value 179.5).[12] Vinyl stearate was prepared commercially from purified stearic acid by direct vinylation and crystallized from three volumes of acetone. Its iodine number was 80.0 (theoretical value 81.7). In both cases the sample material was received in the form of a fine, white powder as precipitated from solution; samples were prepared by heating to 60°C and casting in a stainless steel mold to give pairs of small discs for testing. Freezing temperatures were found to be 30.5 and 30.9°C for vinyl and ethyl stearate, respectively, when cooled from the melt. Samples of vinyl stearate cooled slowly from the melt to temperatures above 25°C were found to "explode" out of the mold in the form of a white, granular ma-

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[8] J. W. C. Phillips and S. A. Mumford, J. Chem. Soc. **1931**, 1732.
[9] R. Buckingham, Trans. Faraday Soc. **30**, 377 (1934).
[10] V. Vand, Acta Cryst. **1**, 697 (1954).
[11] E. S. Lutton, J. Am. Oil Chemists' Soc. **35**, 11 (1958).
[12] The samples were prepared by W. S. Port of the Eastern Utilization Research Branch of the Agricultural Research Service of the U. S. Department of Agriculture, Philadelphia, Pennsylvania.

TABLE I. Sample dimensions.

Material	Vinyl stearate (A)	Vinyl stearate (B)	Ethyl stearate
Sample No.	42	45	47
Dimensions			
Diameter (in.)	0.500	0.375	0.375
Thickness (in.)	0.125	0.200_1	0.188_3
			0.187_8
Sample coefficient[a] (cm)	7.98	2.80	2.98
Weight (g)	0.387_0	0.346_0	0.319_8
	0.382_8	0.347_0	0.316_1

[a] $A_1/h_1 + A_2/h_2 \cong 2A/h$ where A is the cross-sectional area and h the thickness of each sample.

terial full of cavities, not suitable for mechanical tests. However if the liquid vinyl stearate was quenched by cooling from 60 to 15°C within 5 minutes a compact, semitranslucent, waxy material was obtained which was suitable for dynamic measurements. After a long time at room temperature (~25°C) these samples become increasingly opaque with white regions visible throughout their generally cloudy volume. These observations naturally lead to the conclusion that at least two (and perhaps more) crystalline forms are possible.

The behavior of the ethyl stearate upon freezing was in agreement with previous observations,[6,7,8,13] i.e., at 30.9°C the liquid became a soft, transparent solid which changed instantly to a white, opaque (and less plastic) solid at 25.5°C. The change observed at 25.5°C was not reversible. This particular transition has been attributed to a tilt of the stearate chain with respect to the crystal planes formed by the terminal groups in the lower (β) form while the chains are vertical to these planes in the high temperature (α) form. A corresponding difference is found in the long spacing from x-ray diffraction[6] as the distance between planes is 28.6 A for the α form and 25.5 A in the β form.

A summary of sample dimensions is given in Table I.

III. EXPERIMENTAL METHODS

1. Volume Expansion and Cooling Curves

In order to locate transition points several cooling curves were obtained for both vinyl and ethyl stearate. The method consisted of placing about 3 cc of liquid sample (at 50°C) in a 5-cc test tube with a two-junction iron-constantan thermocouple (No. 30 B and S gauge wire) in the center. The test tube was placed in an insulated container and immersed in a water bath which was regulated so that the ambient temperature in the air space surrounding the test tube dropped at the rate of approximately 0.2°C per minute. A Rubicon[14] potentiometer and pointerlite galvanometer were used

to determine the emf between the junctions in the sample and reference junctions kept at 0°C. By comparison with a standard thermocouple calibrated by the National Bureau of Standards the thermocouple was found to be within ±0.1°C (equal to the precision of measurement). Temperature readings of the samples were taken every minute and the ambient temperature read (by means of a second thermocouple) every two or three minutes.

A mercury dilatometer[15] was used to determine the density of vinyl stearate at various temperatures between 50 and 15°C. The dilatometer bulb was immersed in water in an unsilvered Dewar flask so that the appearance of the sample could be noted; a mercury thermometer with scale divisions of 0.1°C was placed in the Dewar near the dilatometer bulb and used to indicate the sample temperature under equilibrium conditions. The sample was put in the dilatometer in liquid form and thoroughly degassed by alternately freezing and melting it under a vacuum (10^{-3} mm Hg) to remove all dissolved air or other gases. Degassed, clean mercury was then added and the dilatometer bulb connected to a 2-mm precision bore capillary in which the height of the mercury column could be read to within 0.01 mm by means of a cathetometer. For vinyl stearate this meant that changes in density of the order of 5×10^{-4} g/cc could easily be determined within ±2%. All readings were taken under equilibrium conditions, i.e., a series of cathetometer readings was taken at each temperature until two readings taken from one to two hours apart were the same. At the freezing point, for example, twenty-five hours were required for an equilibrium height to be reached.

2. Shear Compliance Measurements

Complex shear compliance measurements were made by means of an electromagnetic transducer apparatus previously described.[1,16] In this apparatus a pair of samples is clamped between metal surfaces and sheared by a sinusoidally varying stress in a direction perpendicular to the static clamping stress. Readings of resistance and capacitance of an electrical bridge circuit at balance are used to calculate the storage compliance J' (defined as the amplitude of the strain component in phase with the stress divided by the amplitude of the stress) and the loss compliance J'' (defined as the amplitude of the strain component 90° out of phase with the stress divided by the stress amplitude) with a precision of ±3%. J' is a measure of the elastic response or energy stored per cycle while J'' is proportional to the viscous part of the response or energy loss per cycle. The ratio J''/J' is proportional to the reciprocal Q or logarithmic decrement obtained in internal friction

[13] W. O. Baker and C. P. Smyth, J. Am. Chem. Soc. 60, 1229 (1938).

[14] Rubicon Company, Philadelphia, Pennsylvania.

[15] The dilatometer was provided through the courtesy of W. Webb and R. R. Nelson. A description of it is given in the thesis of R. R. Nelson submitted in January 1959 in partial fulfillment of the requirements for the Ph.D. degree at The Pennsylvania State University.

[16] E. R. Fitzgerald and J. D. Ferry, J. Colloid Sci. 8, 1 (1953).

measurements. Static clamping stresses vary from 10^6 to 10^7 dynes/cm^2 ($\sim$15 to 150 psi) while the dynamic stress amplitudes are always less than 5×10^3 dynes/cm^2 ($\sim$0.08 psi) resulting in strain amplitudes of 10^{-5} to 10^{-7} depending on the sample dimensions and properties. All of the results were for strains small enough so that compliance changes with strain amplitude were less than 0.1% over a twofold range in strain.

Sample temperatures are determined by a two-junction copper-constantan thermocouple located within 0.025 in. of the samples. The precision of temperature readings is ±0.05°C; comparison of the thermocouple with one calibrated by the National Bureau of Standards revealed no differences greater than 0.1°C.

IV. EXPERIMENTAL RESULTS

1. Cooling and Heating Curves

Typical cooling curves for vinyl and ethyl stearate are shown in Fig. 1. Vinyl stearate exhibited a small bump in its cooling curve at 32.6–33.1°C for four different sets of measurements so that some sort of liquid-liquid transition may take place in this region. At this temperature the sample also changed from a clear to a cloudy liquid. The freezing point, represented by the temperature at which the long plateau occurs,
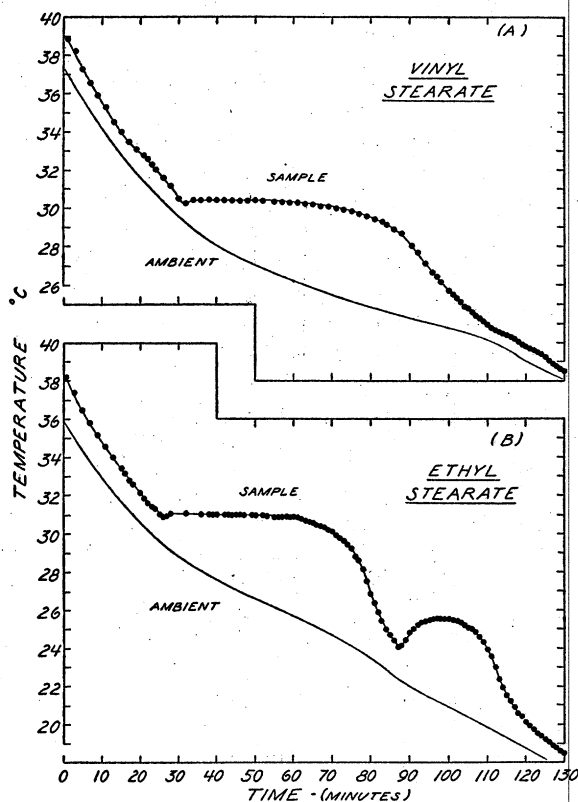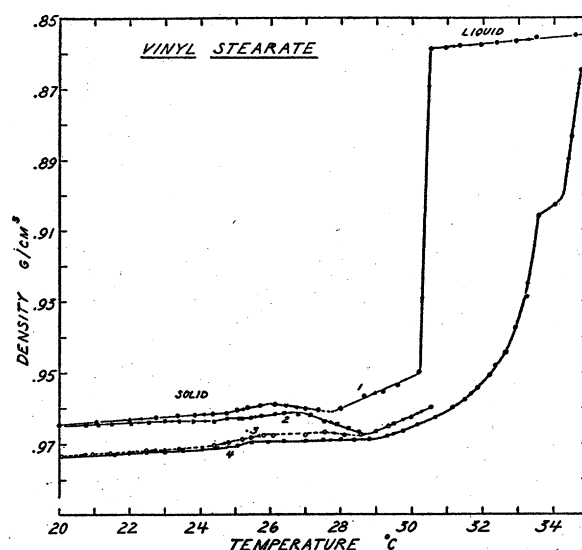

FIG. 2. Temperature dependence of density for vinyl stearate; crystallization point 30.5°C. Descending temperatures, curves 1 and 3; ascending temperatures, curves 2 and 4.

was found to be 30.5±0.1°C in each case. At this temperature the sample changed from a milky or cloudy liquid to a white, opaque solid. Heating curves for vinyl stearate revealed a more gradual transition from solid to liquid giving a melting point between 31.2 and 33.2°C.

Two cooling curves were obtained for the sample of ethyl stearate giving a freezing point of 30.9°C in each case. No change in the slope or appearance was noted while the sample was a liquid. From 30.9 to 25.5°C a clear, transparent solid was present but at 25.5°C a change to a white, opaque material was noted. This corresponds to a small plateau (preceded by supercooling to 24.1°C) observed in the cooling curves [see Fig. 1(B)]. A heating curve from 16 to 45°C showed no solid-solid transition but only a long plateau from which a melting point of 33.2°C was obtained. The results for ethyl stearate are in substantial agreement with those reported by previous investigators[6–8]; the cooling curve plateau at 25.5°C corresponds to the irreversible α, β transition previously mentioned.

2. Temperature Dependence of Density

Cooling curves do not yield information on second-order transitions or first-order transitions which occur very slowly. In order to search for possible transitions in vinyl stearate not revealed by the cooling or heating curves equilibrium measurements of density—temperature were carried out as described in Part III. A portion of the density temperature curve for vinyl stearate is shown in Fig. 2. Measurements were started with the vinyl stearate in the form of a clear liquid at 40°C and continued down to 15°C (curve 1). At 32–33°C the liquid became cloudy and at 30.5°C began to crystallize. The temperature was held at 30.25°C for twenty-five

FIG. 1. Cooling curves: (A) vinyl stearate; crystallization point 30.5°C, no evidence of a solid-solid transition; (B) ethyl stearate; crystallization point 30.9°C, α–β transition at 25.5°C.
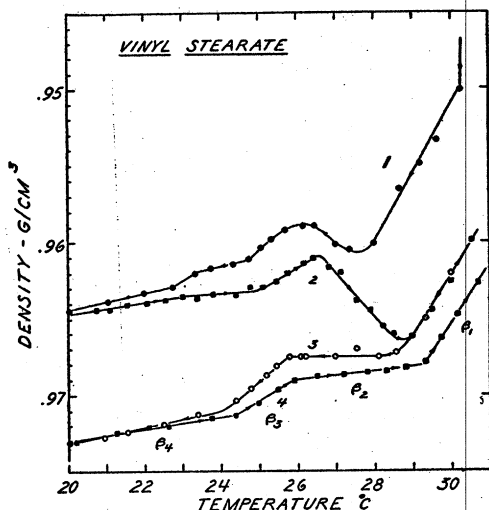
FIG. 3. Enlarged plot of density-temperature curves from Fig. 2 showing second order solid-solid transitions in vinyl stearate. Curve 4: β_4, β_3 at 24.4°C; β_3, β_2 at 25.9°C; β_2, β_1 at 29.2°C.

hours before the crystallization was complete and the dialatometer readings became constant with time. Below 30.25 five different slopes were observed with transition temperatures of 27.7, 26.1, 24.7, and 23.0°C. Measurements with increasing temperature from 15 to 30.5°C again revealed five slopes (curve 2) with transitions at 23.0, 24.9, 26.5, and 28.7°C. A third, descending run (curve 3) from 30.5 to 17.0°C gave four slopes with transitions at 28.7, 25.8, and 24.1°C. A final, ascending run showed four different slopes in the solid state with transitions at 24.3, 25.9, and 29.2°C. An additional set of measurements with rising and falling temperatures taken before curve 4 fell between curves 3 and 4. The existence of different crystalline forms in the solid state is also evidenced by the density changes occuring in remelting. The first melting occurs between 31.3 and 33.6°C (corresponding closely to the heating curve results mentioned in part 1 of this section). A second melting then occurs between 34.2 and 34.8°C, while a third transition (not shown in Fig. 2) occurs at 36.7°C. The vinyl stearate appeared to be a grayish solid or semisolid between 31.3 and 34.8°C but above this temperature portions of clear liquid were visible. The entire sample became clear at about 40°C.

The solid-solid transitions are shown more clearly in the enlarged plot of Fig. 3 where the four slopes finally obtained are identified with possible β_1, β_2, β_3, and β_4 crystalline states. The entire set of density measurements extended over a period of 51 days. A summary of the results of both cooling curve and density measurements is given in Table II.

3. Frequency Dependence of Compliance for Vinyl Stearate

Measurements of shear compliance on sample A of vinyl stearate at 25.7°C made from 100 to 5000 cps

within 2 to 100 hr after formation from the melt showed only one substantial resonance, at 3070 cps. At 19.1°C measurements from 100 to 4000 cps revealed no change in the 3070 cps resonance but a few additional, small resonances were more noticeable than at 25.7°C. The sample was kept in the apparatus at temperatures between 24.5 and 27.5°C for 1504 hr (about 62 days) and then remeasured at 25.5°C. A huge resonance was now found at 360 cps. Values of J'' increased from about 0.02×10^{-9} cm²/dyne off resonance to 95.0×10^{-9} cm²/dyne at the resonant frequency. Additional, smaller resonances were found at nine other frequencies between 500 and 4000 cps. As the temperature was lowered to 13.5, −1.3, and −27.8°C the large resonance broke up into a triplet so that at −27.8°C, for example, there were resonances at 300, 340, 435 cps with maximum values of loss compliance (J'') of 224, 27, and 7.0×10^{-9} cm²/dyne, respectively. The number of additional resonances between 1400 and 4000 cps increased from seven at 24.5°C to ten at −28.3°C and various changes in magnitude occured as well. These results are summarized in Table III.

A second set of samples (B) of vinyl stearate was prepared in the same manner as A but instead of waiting a long time at room temperature the temperature was lowered to 14, −1.4, and −28°C within 800 hr after the samples were formed. Some of the results are shown in Figs. 4–8. Starting at 25.1°C (Fig. 4) there are no resonances from 100 to 1000 cps and only a few very small peaks from 1000 to 5000 cps; the largest of these is at 1005 cps and reaches a maximum value of J'' of only 0.70×10^{-9} cm²/dyne. When the temperature was lowered to 14.2°C, however, a huge resonance appeared at 300 cps. This is shown in Fig. 5 where values of compliance from 100 to 1400 cps are plotted on a greatly reduced scale in order to show the maximum in loss compliance of approximately 65.0×10^{-9} cm²/dyne. It is worth noting that the data of Fig. 4 plotted to the scale of Fig. 5 would show as a horizontal line at the zero level. Additional resonances were found between 1400 and 5000 cps at this temperature, one having a loss compliance maximum of about 8.0×10^{-9} cm²/dyne at 1975 cps, another with a maximum of 1.3×10^{-9} cm²/dyne at 1675 cps and the rest, maxima less than 0.5×10^{-9} cm²/dyne.

At −1.4°C the spectrum remained almost the same as at 14.2°C; a large resonance occurred at 320 cps ($J_{max}'' = 45 \times 10^{-9}$ cm²/dyne); and a smaller one at 1975 cps ($J_{max}'' = 16 \times 10^{-9}$ cm²/dyne). At −28.4°C a triplet appeared as shown in Fig. 5. The triplet resonances occured at 200, 230, and 285 cps with maximum values of loss compliance of 70, 28, and 18×10^{-9} cm²/dyne respectively.

The sample was subsequently returned to 24.9°C and remeasured from 100 to 1400 cps. Only one small resonance was found with a maximum value of loss compliance of 1.0×10^{-9} cm²/dyne at 970 cps. The temperature was again lowered to 14.0°C and measure

TABLE II. Summary of thermal measurements.

		Cooling curves[a]		
	Material	Freezing point °C	Solid-solid transitions °C	Melting point °C
	Vinyl stearate	30.5±0.1	none observed	31.2–33.2
	Ethyl stearate	30.9±0.1	25.5±0.1	33.2±0.1

		Density-temperature curves		
Vinyl stearate	Freezing point °C ±0.1	Solid-solid transitions °C ±0.1	Density-temperature coefficient 10^{-3} g/cm^3 °C	Melting point °C ±0.1
Descending (1)	30.5	27.7	−3.9 (30.2 to 27.7)	
			+2.0 (27.7 to 26.1)	
		26.1	−2.1 (26.1 to 24.7)	
		24.7	−0.70 (24.7 to 23.0)	
		23.0	−0.60 (23.0 to 15.0)	
Ascending (2)		28.7	−3.9 (30.6 to 28.7)	
			+2.8 (28.7 to 26.5)	
		26.5	−1.4 (26.5 to 24.9)	
		24.9	−0.21 (24.9 to 23.0)	
		23.0	−0.40 (23.0 to 15.0)	
Descending (3)		28.7	−3.9 (30.5 to 28.7)	
			−0.0 (28.7 to 25.8)	
		25.8	−2.0 (25.8 to 24.1)	
		24.1	−0.46 (24.1 to 20.0)	
Ascending (4)		29.2	−3.9 (30.7 to 29.2)	31.3–33.6
			−0.30 (29.2 to 25.9)	
		25.9	−0.92 (25.9 to 24.3)	34.2–34.8
		24.3	−0.42 (24.3 to 20.0)	36.7

[a] Identical results were obtained for two sets of measurements.

ments from 100 to 1400 cps revealed an enormous resonance at 310 cps. A summary of results on sample B is given in Table IV.

4. Compliance Measurements on Vinyl Stearate above and below 24.8$_5$°C

As a result of the measurements just described it became obvious that a transition affecting the mechanical properties of sample B was occurring between 14 and 25°C. Hence a series of measurements was instituted to close in on the transition temperature; these were confined to the frequency range from 50 to 600 cps and yielded the following results in the order given: at 23.8$_3$°C the large resonance was present at 300 cps; at 25.0$_7$°C no resonances were present; at 24.3$_0$°C the large resonance reappeared at 305 cps; at 25.1$_0$°C it disappeared again. These remarkable results are adduced in Fig. 7.

Finally, measurements in the vicinity of the resonance peak (295–305 cps) were made as the temperature of the sample was slowly raised from 24.6 to 25.2°C and then lowered to 24.6°C again. From these measurements a transition temperature between 24.7$_1$ and 25.0$_0$ was deduced; the mean value was set at 24.8$_5$°C as shown in Fig. 8.

5. Changes in the Compliance of Vinyl Stearate with Time

It has already been pointed out that after 1677 hr at room temperature sample A of vinyl stearate showed a very large resonance at 360 cps. (Sec. 3 and Table III). Since no measurements were made on sample A between 173 and 1677 hr the exact time at which this resonance appeared could not be determined. Sample B was measured at 25.1°C at 1415 hr after forming from the melt and had no resonance between 50 and 600 cps. At 1462 hours, however, the same resonance (305 cps) previously found only below 24.8$_5$°C was now found at 25.1°C in sample B. Measurements at 1606 and 1773 hr at 25.3 and 25.4°C confirmed the continued existence of the resonance. Thus it appeared that the state of the sample occurring initially only below 24.8$_5$°C was also attained with time at higher temperatures, and was the final or stable state at room temperature. (see Table IV). The results on B are therefore in essential agreement with those on A.

6. Effect of Static Stress on Compliance Spectrum of Vinyl Stearate

Previous measurements on polyvinyl stearate[3] demonstrated that the positions and magnitudes of me-

TABLE III. Summary of mechanical resonances in sample A of vinyl stearate at various times and temperatures.

Time after crystallization from melt (hr)	Temp °C	Resonant frequencies (cps)	Loss compliance maxima, J_{max}'' 10^{-9} cm²/dyne	Range (cps)
2–100	25.7	1520	0.10	100–5000
		3070	4.4	
		3240	0.10	
122–173	19.1	1540	0.45	100–4000
		2840	0.32	
		3070	4.	
		3670	0.20	
1677–1853	25.5	360	95.0	100–1400
		550	2.5	
		625	2.5	
	24.5	1510	1.2	1400–4000
		1895	1.3	
		2040	2.1	
		2315	0.60	
		2930	0.65	
		3325	0.30	
		3840	0.25	
	13.5	420	200	50–1400
		475	32	
		615	1.6	
	14.5	1515	1.6	1400–4000
		1835	3.8_5	
		1955	2.9	
		2465	0.30	
		2890	0.15	
		3285	1.3	
		3870	0.60	
2330–2356	−1.3	350	∿200	50–1400
		405	18	
		510	3.5	
		1340	0.20	
	−2.2	1510	1.45	1400–4500
		1620	0.50	
		1750	4.5	
		1860	0.55	
		1940	0.35	
		1970	0.25	
		2245	0.60	
		3250	1.4	
		3900	0.50	
2691–2832	−27.8	300	224	50–1400
		340	27	
		435	7.0	
		1340	0.30	
	−28.3	1510	2.25	1400–4000
		1640	2.9	
		1695	3.0	
		1770	0.90	
		1970	0.15	
		2110	0.35	
		3160	0.65	
		3220	0.65	
		3670	0.20	
		3890	0.50	

chanical resonances were altered by changes in static clamping stresses. Therefore a very slight increase in static stress (corresponding to one-quarter turn of the sample holder screw[1]) was applied to sample B at the conclusion of the measurements described in the previous section. With the increased pressure only one resonance was observed in the 100 to 4000 cps region; at 2940 cps. The peak value of loss compliance at this frequency was about 1.8×10^{-9} cm²/dyne. The spectrum everywhere else was absolutely flat. Subsequently the static pressure was reduced to approximately its initial value and with this a large resonance reappeared, now at 195 cps with a loss compliance maximum of 100×10^{-9} cm²/dyne, and accompanied by a smaller reso-
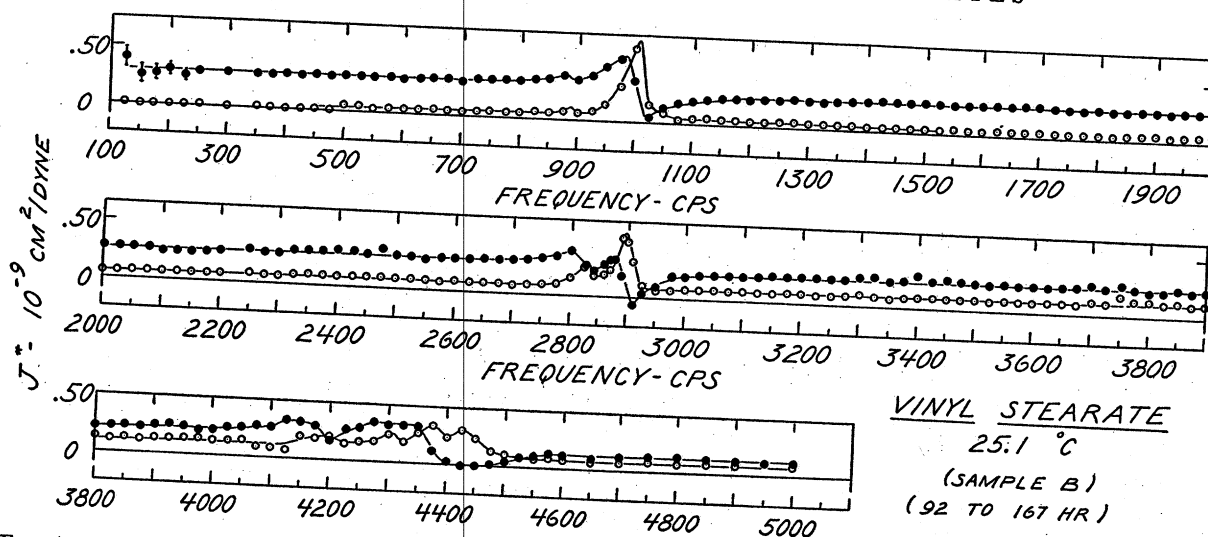
FIG. 4. Variation of complex shear compliance $(J^*=J'-iJ'')$ with frequency for vinyl stearate (sample B) at 25.1°C and 92 to 167 hours after crystallization from the melt. Solid points, J'; open points, J''.

nance at 325 cps $(J_{max}''=10\times10^{-9} \text{ cm}^2/\text{dyne})$. With increasing time the resonance moved to higher frequencies and decreased in magnitude. A summary of these measurements (confined to the 50 to 600 cps region) is given in Table V.

7. Compliance Measurements on Ethyl Stearate

Samples of ethyl stearate quenched to 15°C from the melt and then warmed to 24.2°C were measured within a few hours after formation (2.2 to 10.8 hr) and found to have only one very small resonance at 1100 cps $(J_{max}''=0.516\times10^{-9} \text{ cm}^2/\text{dyne})$ in the frequency range from 50 to 1200 cps. From 1200 to 2560 cps no resonances were found but between 29.5 and 69.2 hours the levels of J' and J'' increased. That is, values of compliance at 2175 cps at 29.5 hr were 0.270 and 0.030$\times$ 10^{-9} cm²/dyne for J' and J'' respectively but at 69.2 hr were 0.335 and 0.055$\times10^{-9}$ cm²/dyne at the same frequency! Subsequently at 172.2 to 195.5 hr values of compliance from 50 to 1400 cps were obtained revealing resonances at 275, 320, and 420 cps with maximum values of loss compliance of 80, 5.5, and 1.0$\times10^{-9}$ cm²/dyne, respectively. The results at 2.2 and 172.2 hr are compared in Fig. 9. Measurements from 50 to 600 cps made at later times (up to 1200 hr) showed that the resonance first observed at 172.2 hr remained at practically the same frequency, but the level of J_{max}'' at 275 cps rose to around 100$\times10^{-9}$ cm²/dyne while the maximum value of loss compliance of the third resonance rose from 1.0 to 3.0$\times10^{-9}$ cm²/dyne. Resonances were also found at 1500, 1705, 1845, and 2990 cps. The results are summarized in Table VI. It should be pointed out that results at 26.8°C were the same as those at 24.2°C. It was originally intended to drop the temperature to 15°C as was done for sample B of vinyl stearate but the appearance of resonances in ethyl stearate occured before initial meaurements at room

temperature could be completed, (i.e., after 69 instead of 1462 hr).

V. DISCUSSION

1. Crystalline Modifications in Long-Chain Hydrocarbon Compounds

The main features of the polymorphism of long chain hydrocarbon compounds can be summarized briefly as follows[6-11]: the compounds crystallize with their end groups in planes and with the hydrocarbon chains either perpendicular (α form) or tilted with respect to the planes (β form).[6] The α and β forms can be distinguished by their long x-ray spacings which are smaller in the β than in the α form and by the fact that the α form is generally transparent and the β form is opaque. The α forms (perpendicular chains) can be further classified according to the cross-sectional arrangement of the chains in hexagonal or rectangular arrays. The β forms (tilted chains) can be subdivided, in turn, according to the angle of tilt, or the cross-sectional spacings of the chains. Thus in the α form hexagonal or orthorhombic unit cells are possible while in the β form various monoclinic or triclinic forms can exist. A further distinction is made according to the relative orientation of the planar zigzag carbon chains with respect to each other. These may be randomly oriented (freely rotating, e.g., in the α hexagonal form), alternate rows may be parallel, or all zigzag planes may be lined up in the same direction. Classification according to the carbon plane orientation is particularly useful in connection with dielectric measurements where increased contributions to the polarization occur when dipole groups are attached to the rotating chains. It is not necessarily true, however, that this type of rigid chain rotation or oscillation produces an increased mechanical compliance. In fact the large mechanical resonance dispersions and increased compliances re-
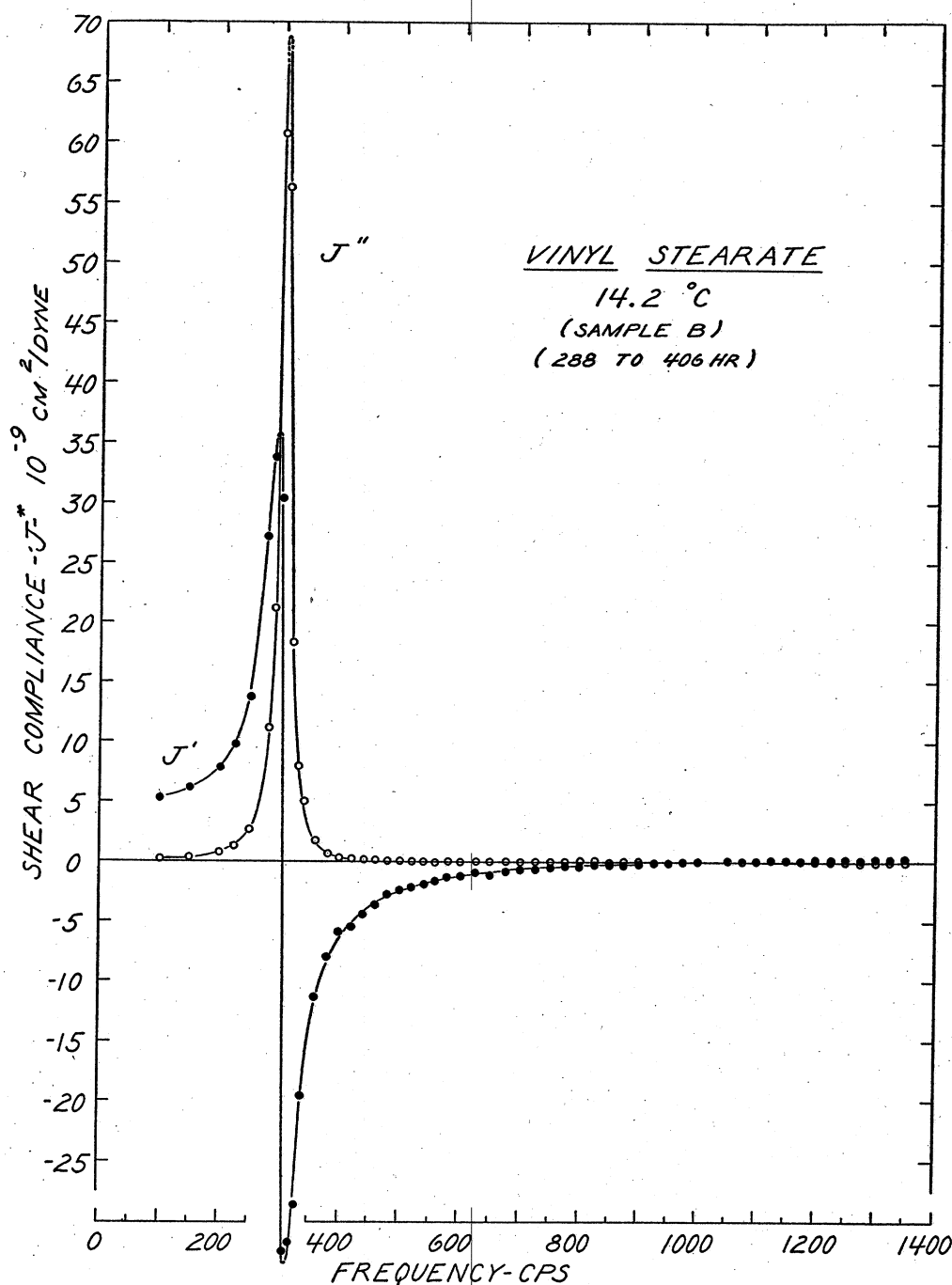
FIG. 5. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for the vinyl stearate of Fig. 4 (sample B) at 14.2°C. Note that the scale is greatly reduced compared to Fig. 4. Solid points, J'; open points, J''.

ported here are observed for vinyl and ethyl stearate in the stable or β form while specific heat,[17] dielectric constant,[9] and nuclear magnetic resonance[18] measurements indicate that rotation takes place chiefly in the α forms of these types of esters.

Various modifications of structure have been reported for ethyl esters in both the perpendicular (α) and tilted (β) forms. Ethyl behenate, for example, has two α

and two β forms according to the density and dielectric constant measurements of Buckingham[9]; the liquid solidifies into an α_1 form at 47°C and then undergoes an irreversible transition into α_2 at 45°C. In both α forms the long spacing is 33.9 A. At 43°C an irreversible transition into a β_1 form occurred and at 30°C a reversible transition into a β_2 form was observed. Both β forms gave a long spacing of 30.1 A. As the temperature was subsequently raised and lowered around 30°C, however, the change in slope of the density vs tempera-

[17] Garner, Van Bibber, and King, J. Chem. Soc. 1931, 1533.
[18] E. R. Andrews, J. Chem. Phys. 18, 607 (1950).

FIG. 6. Variation of complex shear compliance ($J^* = J' - iJ''$) with frequency for the vinyl stearate (sample B) at $-28.4°$C. Same scale as Fig. 5. Solid points, J'; open points, J''.
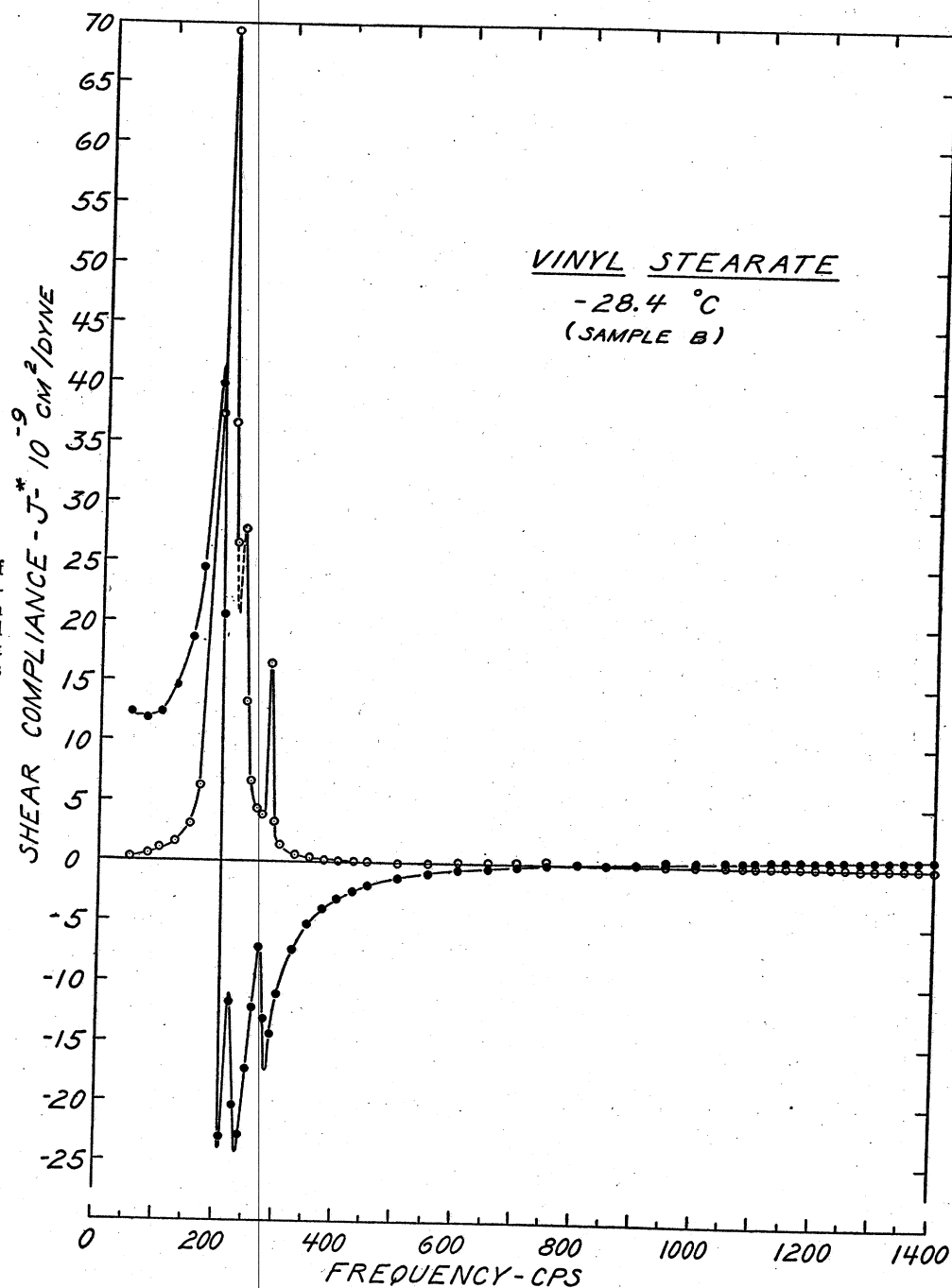
ture curve at 30°C became less pronounced, until it was finally very slight. This behavior of ethyl behenate is similar to that observed for vinyl stearate in the present investigation (see Fig. 3) where density measurements indicate four β forms. The temperature density coefficient for the β_1 and β_4 forms remains unchanged but after each heating cycle the β_2–β_3 transition becomes less pronounced. Unfortunately no x-ray measurements have been reported for vinyl stearate although Malkin[19]

has reported both long and short spacings for ethyl stearate in a β form which indicate a monoclinic structure of the type shown in Fig. 10. Powder diffraction patterns of vinyl stearate cooled from the melt were obtained at six temperatures between 30 and 22°C and at 0°C in the present work, but no changes were observed by this method.[20] Thus it appears that the crystalline transitions occurring in vinyl stearate between 24 and 30°C are monoclinic to monoclinic, or

[19] T. Malkin, *Progress in the Chemistry of Fats* (Academic Press Inc., New York, 1952), Vol. 1, Chap. 1.

[20] The x-ray diffraction patterns were obtained through the courtesy of K. Vedam and B. B....
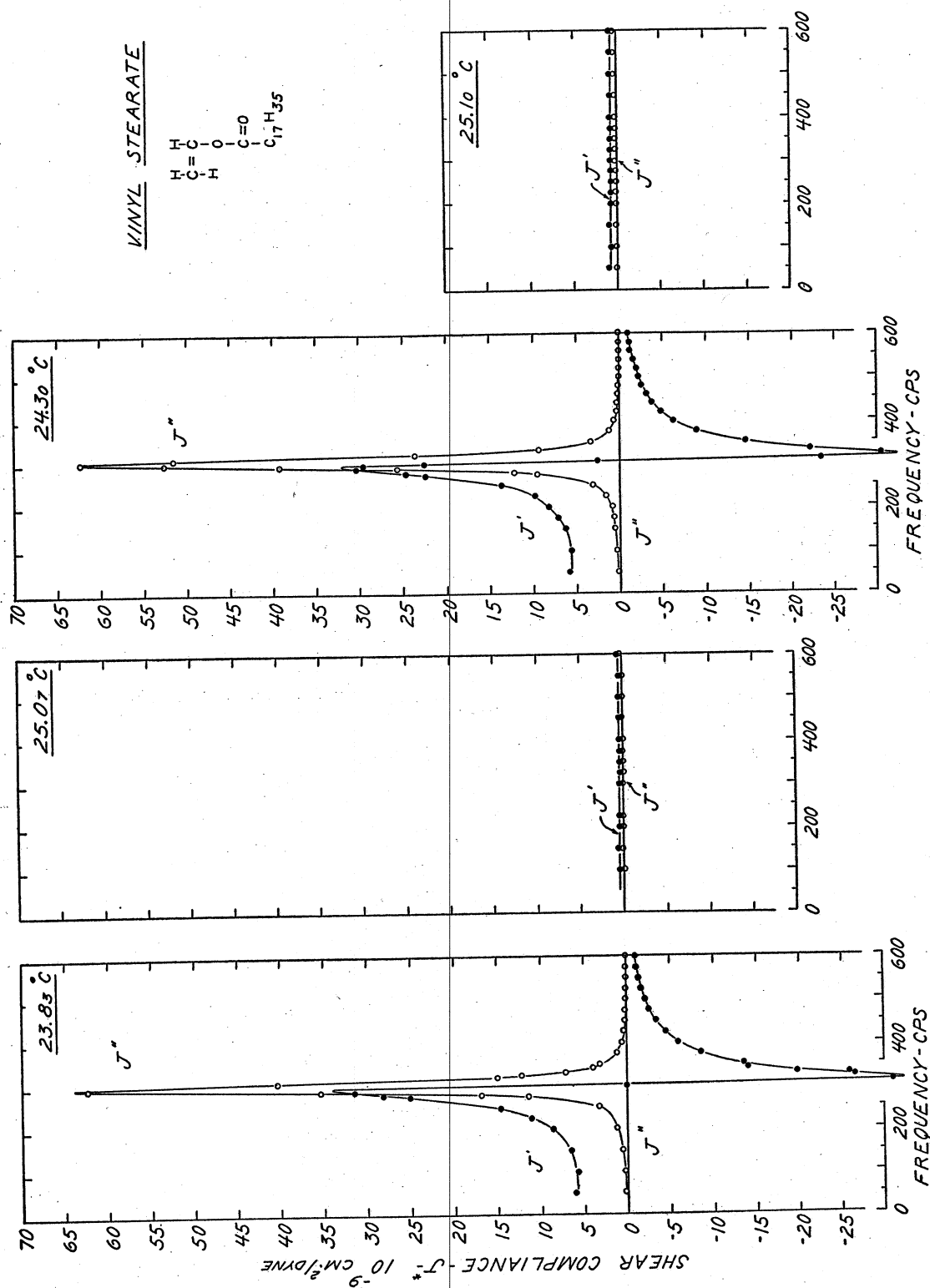
FIG. 7. Variation of complex shear compliance ($J^* = J' - iJ''$) with frequency for vinyl stearate (sample B) below and above the transition point at 24.8°C; same scale as Fig. 5. Solid points, J'; open points, J''.

monoclinic to triclinic, etc., where the long (c) spacing is unchanged.

Changes in crystal structure with time have also been noted for ethyl esters[6] and other long chain compounds; the α (hexagonal or orthorhombic) forms are often metastable and change slowly to the β form even at temperatures above the normal transition point.[13] The presence of a few percent of impurities of neighboring homologs has been found to make the α form of normal hydrocarbons stable[21] and to delay the transition to the β form[7] in ethyl stearate. The fact that changes in crystal structure may occur very slowly with time is of interest here since in both ethyl and vinyl stearate marked changes occur in the dynamic mechanical properties between 29.5 and 69.2 hr and 1415 to 1462 hr, respectively, after crystallization from the melt.

2. Effect of Crystalline Transitions on Mechanical Resonances

The remarkable changes in dynamic shear compliance which occured with time after the samples were formed from the melt can be tentatively ascribed to a change from a metastable state (possibly a mixture of two forms) to a stable form in which the observed mechanical resonance can occur. Thus both samples of vinyl stearate and the ethyl stearate initially showed only a few very small resonances and none between 50 and 600 cps. However after some time at room temperature tremendous resonances appeared permanently at 360, 305, and 275 cps for samples A and B of vinyl stearate and ethyl stearate, respectively. Since slight differences in static pressure can shift resonance peaks considerably[3,5] these resonances are sufficiently close in frequency and magnitude to be attributed to the same mechanism. Another similarity is that in sample B of vinyl stearate and in ethyl stearate when the large peaks were not present there were small resonances near 1000 cps, but whenever the large peaks near 300 cps appeared the ones near 1000 cps disappeared.

The most striking feature of the results is the appearance and disappearance of a tremendous resonance below and above 24.8_5°C as described in Sec. 4 of Part IV and shown in Fig. 7. This effect was completely reversible and reproducible for 1415 hr (about 58 days) during which time the transition point was crossed repeatedly and always with the same result: below 24.8_5°C a large resonance was present near 300 cps (along with many others at higher frequencies); above 24.8_5°C this resonance (and the others) disappeared. During this time the level of the compliance values above the transition (with no resonance) were steadily increasing, e.g., J' increased from 0.30×10^{-9} cm²/dyne at 120 hr to 0.65×10^{-9} cm²/dyne at 1412 hr. Since the density-temperature curves for vinyl stearate indicate a β_3 to β_4 transition occurring between 25 and

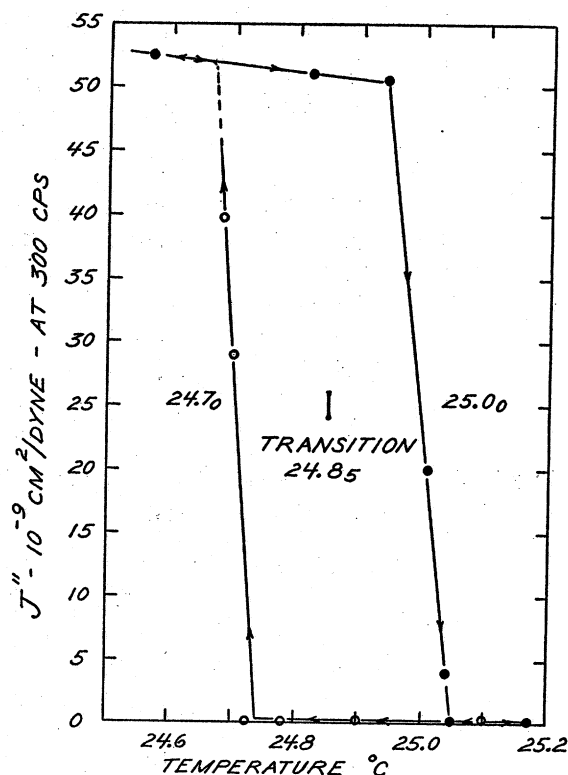[21] A. E. Smith, J. Chem. Phys. **21**, 2229 (1953).

Fig. 8. Values of loss compliance for vinyl stearate (sample B) at 300 cps for ascending and descending temperatures in the vicinity of the transition at 24.8_5°C.

24°C (see Fig. 3) the changes in mechanical behavior could be connected with this transition; the resonance occurring in the β_4 form but not in β_3. Furthermore it appears from the data of Fig. 3 as if the β_2–β_3 and β_3–β_4 transitions might eventually disappear as was the case for the β_1–β_2 transition in ethyl behenate reported by Buckingham.[9] This would leave the vinyl stearate in the β_4 form and account for the fact that after 1415 hr the resonance remained, even with the sample at temperatures above the (temporary) transition point.

3. Analysis of Low-Frequency Resonance in Vinyl Stearate

Although a number of resonances occur when vinyl stearate is in the β_4 form it seems reasonable to concentrate attention at first on the large resonance near 300 cps. If some explanation can be found for its occurrence an understanding of the other resonances should be possible. Resonance dispersions of this kind have been fitted by assuming a generalized stress-strain relationship of the form[4,5]

$$s = k_0 a + k_1 (da/dt) + k_2 (d^2 a/dt^2) \qquad (1)$$

where s is the stress, a the strain, and k_0, k_1, and k_2 are constants. Then for a sinusoidal stress of circular frequency ω it can be established that the components

TABLE IV. Summary of mechanical resonances in sample B of vinyl stearate at various times and temperatures.

Time after crystallization from melt (hr)	Temp °C	Resonant frequencies (cps)	Loss compliance maxima, J_{max}'' 10^{-9} cm²/dyne	Range (cps)
120–137	25.1_6	none	...	100–600
137–139	24.9_8	none	...	600–1000
92.5–113	25.4_0	1005 2830	0.70 0.25	1000–2800
113–118	24.9_0	2895	0.55	2800–3400
118–119	25.1_0	none	...	3400–4000
141–167	24.9_8	4200 4300 4380 4425	0.20 0.25 0.30 0.30	4000–5000

The foregoing data are plotted in Fig. 4 where the mean temperature is given as 25.1°C

Time after crystallization from melt (hr)	Temp °C	Resonant frequencies (cps)	Loss compliance maxima, J_{max}'' 10^{-9} cm²/dyne	Range (cps)
288–454	14.2	300 1675 1900 1975 2145 2160 3310 3590 3710 3890 4620	65–66 1.3 0.50 8. 0.20 0.25 0.20 0.30 0.15 0.20 0.30	100–5000
599–620	−1.4	320	45	100–1400
	−1.9	1685 1910 1975 2190 2240	0.30 0.45 ∿16 0.10 0.10	1400–2800
759–816	−28.4	200 230 285 1590 1735 1870 2590 2635 2770	70. 28. ∿18. 1.0 0.35 ∿2.5 0.20 0.3 0.3	50–2800
1095–1104	24.9	970	∿1.0	100–1400
1170–1176	14.0	310	∿67	100–1400
1245–1247	23.8_3	300	65–67	50–600
1275–1277	25.0_7	none	...	50–600
1290–1293	24.3_0	305	64–66	50–600
1412–1415	25.1_0	none	...	50–600
1462–1464	25.1_0	305	65–67	50–600
1606–1609	25.3_2	305	65–67	50–600
1773–1775	25.4_0	305	65–66	50–600

of complex shear compliance are

$$J' = J_a' + (1/k_0)\{(1-\omega^2/\omega_r^2)/[(1-\omega^2/\omega_r^2)^2+\omega^2\tau^2]\}, \quad (2)$$

$$J'' = J_a'' + (1/k_0)\{\omega\tau/[(1-\omega^2/\omega_r^2)^2+\omega^2\tau^2]\}, \quad (3)$$

where $\tau = k_1/k_0$, $\omega_r = (k_0/k_2)^{\frac{1}{2}}$, and J_a' and J_a'' take into

account possible background compliances. Figure 11 illustrates the exactness with which the experimental data for vinyl stearate can be fitted by these expressions. Values of the constants of Eq. (1) selected to give the fit demonstrated in Fig. 11 are listed in Table VII.

Another interesting feature of the results is the appearance of a triplet resonance at low temperatures in
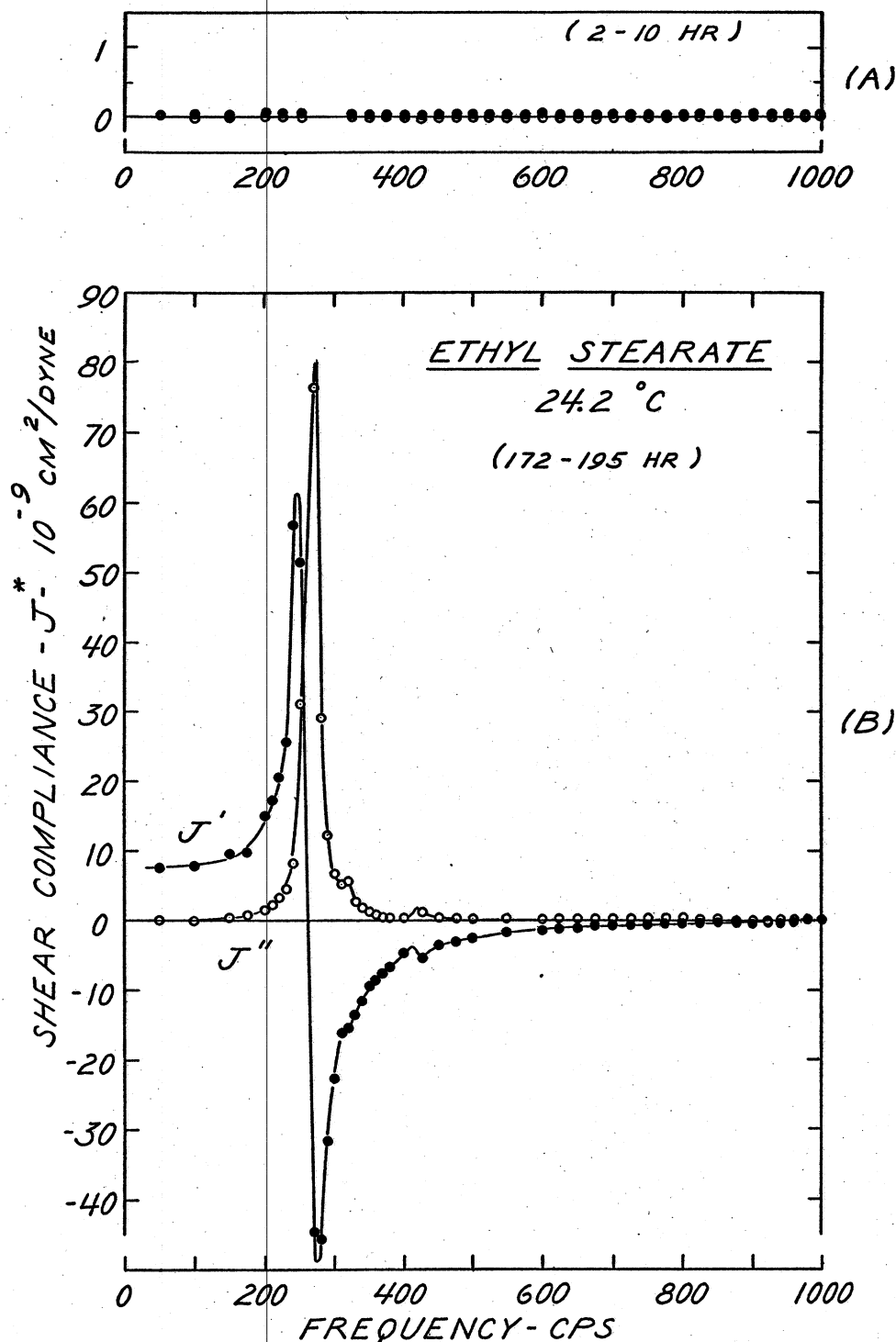
FIG. 9. Variation of complex shear compliance ($J^* = J' - iJ''$) with frequency for ethyl stearate at different times after crystallization from the melt: (A) 2.2 to 10.8 hr; (B) 172 to 195 hr. Scale in (B) reduced to one-half that of Fig. 5 and scale in (A) ten times that of (B). Solid points, J'; open points, J''.

vinyl stearate and at room temperature in ethyl stearate. Two subsidiary resonances appear on the high-frequency side of the main resonance at temperatures of 13.5°C and below in sample A of vinyl stearate; a similar triplet appears at −28.3°C in sample B. The associated resonances decrease in magnitude with increasing frequency and are smallest for ethyl stearate.

The locations of the triplet resonances vary somewhat with temperature, from sample A to sample B of vinyl stearate, and from vinyl to ethyl stearate. The subsidiary frequencies in all cases however appear to be in a fixed ratio to the principal (largest) resonances. Thus if the resonances are denoted as occurring at frequencies f_1, f_2, f_3 where f_1 is the frequency of the principal res-

TABLE V. Changes in mechanical resonances with time after reducing static clamping stress in sample B of vinyl stearate (23.6 to 24.0°C and 50–600 cps).

Static stress change	Time after change (hr)	Resonant frequencies (cps)	Loss compliance maxima 10^{-9} cm²/dyne
Original value	...	305	66
Slight increase	0–219	none	...
Decrease to approximately original value	0–2	175 300	∿150 4.2
	51–54	195 325	∿125 10
	72–76	205 335	∿100 10
	148–150	210 340	81 8.0
	384–386	225 345	70 5.0

onance, the ratios f_2/f_1 and f_3/f_1 are found to be 1.14± 0.02 and 1.48±0.04, respectively, in all cases. These triplet resonances are summarized in Table VIII.

4. Comparison with Polyvinyl Stearate

Large resonances in mechanical compliances have been found also in the range 50 to 600 cps in polyvinyl stearate.[3] A resonance of the same order of magnitude as those reported here ($J_{max}'' \cong 150 \times 10^{-9}$ cm²/dyne) was observed near 200 cps with slight static clamping, and smaller resonances were found at 200 and 500 cps when the static stress was increased. The 500-cps res-

onance disappeared between 30.5 and 36.4°C, probably as a result of a crystalline transition of the type discussed in Sec. 2. The 500-cps resonance was also reduced by increasing the static compression; in one case it was eliminated, but reappeared when the static compression was returned to its initial value. This is, of course, similar to the effect observed for vinyl stearate (Sec. 6, Part V). It seems safe to conclude that the resonances observed in monomer and polymer arise from the same source—whatever that may be.
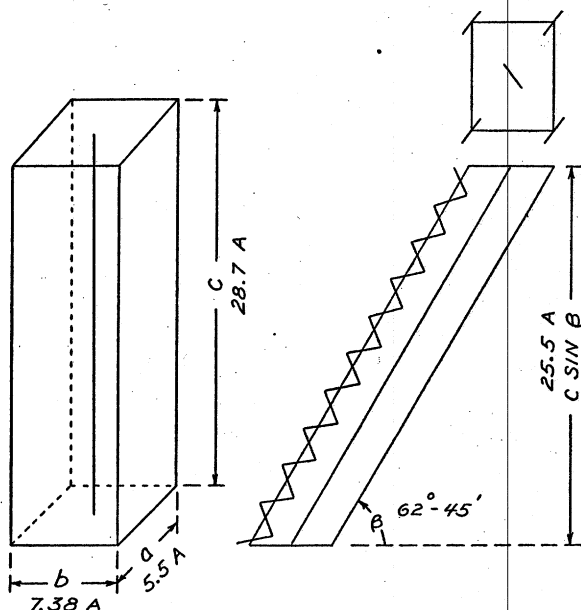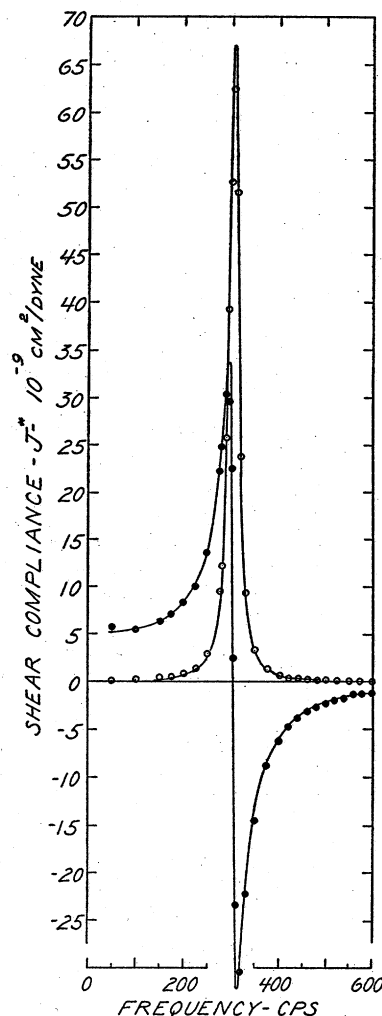

FIG. 11. Comparison of calculated values of compliance based on Eqs. (2)–(3) (solid lines) for the large resonance in sample B of vinyl stearate and experimental results at 24.3°C. Solid points, measured values of J'; open points, measured values of J''. The calculated curves are based on the empirical constants listed in Table VII.

FIG. 10. Possible unit cell for a β form of ethyl stearate based on long and short spacings obtained from x-rays as reported by Malkin.[19]

VI. SPECULATION

In the absence of detailed information on the crystal structures of the various β forms of vinyl stearate it is impossible to draw any firm conclusions as to the exact mechanism responsible for the resonances occuring in the β_4 form. Enough general information about the structure of ethyl esters is available, however, to permit some speculation which might prove useful in planning future experiments or eliminating certain classes of phenomena. As has already been mentioned the fact

TABLE VI. Summary of mechanical resonances in ethyl stearate.

Time after crystallization from melt (hr)	Temp °C	Resonant frequencies (cps)	Loss compliance maxima 10^{-9} cm²/dyne	Range (cps)
2.3–10.8	24.2$_9$	1100	0.52	50–1190
26.8–29.5	24.5$_6$	none	general level 0.030	1200–2175
69.3–71.7	24.3$_5$	none	general level 0.060	2175–2560
172–196	24.2$_0$	275 320 420	~80 5.5 1.0	50–1400
314–318	24.0$_0$	275 320 420	106 5.5 ~2.5	50–600
483–486	24.1$_0$	275 325 430	100 5.5 2.5	50–600
575–576	26.8	275 325 430	100 6.0 ~3.0	50–600

that the large resonance occurs in a β form seems to preclude a direct connection with rotation of the molecule about its chain axis because in this form such rotation is virtually absent. A type of motion which might occur is a rotation of the crystal plane at the top of a small crystalline domain relative to its base in such a way as to maintain the long spacing but change the direction of tilt (orientation) of the domain. In a polycrystalline material consisting of small units oriented at random there must occur many interfaces between the units where the angles of tilt are in opposite directions leaving a diamond shaped void as shown in Fig. 12(a). Either of the neighboring two-domain complexes could then swing around into the void (if swinging space were available) as demonstrated in Fig. 12(b). Such a domain inversion would amount to a precession of the individual tilted chains of the swinging domains [Fig. 12(c)]. Under an alternating stress the domains could swing back and forth or perhaps rotate with an angular frequency ω_D giving rise to a resonance when the applied stress is at the same frequency. As with any model there are many objections to this one, but it is attrac-

tive since a precessional frequency of the sort envisaged could be quite low. For single crystals and other materials without long chains the precession or rotation of edge dislocations could be invoked in a somewhat similar manner.

Perhaps the most straightforward approach is to postulate the existence of certain excited crystalline states with energies very close to the ground state energy for a particular unit cell, and to attribute the absorption resonances to transitions occuring from the ground state to excited states according to certain selection rules as is done for molecular and atomic spectra. The effect of static stress could then be explained in terms of shifts in excited levels, removal of symmetry degeneracies, and so on. Starting with the lattice energy for a crystal, energy levels could be determined assuming each resonance at frequency f_r corresponds to a transition between levels of energy differences hf_r. This would lead to very closely spaced levels (for vinyl stearate, $h300=2.0\times10^{-24}$ erg or 1.2×10^{-12} ev) by the usual standards. Such an analysis is beyond the scope of the present article, however.

TABLE VII. Analysis of dispersion data for the large resonance in vinyl stearate (sample B) at 24.3°C based on Eqs. (2)–(3).

Resonant frequency f_r (cps)	305
Retardation time τ (sec)	$3.5_0\times10^{-5}$
Modulus k_0 (dyne/cm²)	2.2×10^{10}
$1/k_0$ (cm²/dyne)	0.45×10^{-10}
First derivative constant, k_1 (dyne-sec/cm²)	$7.7_7\times10^5$
Second derivative constant, k_2 (dyne-sec²/cm²)	6.0×10^3
Background comp. J_a' (cm²/dyne)	0.45×10^{-9}
J_a''	0

TABLE VIII. Triplet resonances in vinyl and ethyl stearate.

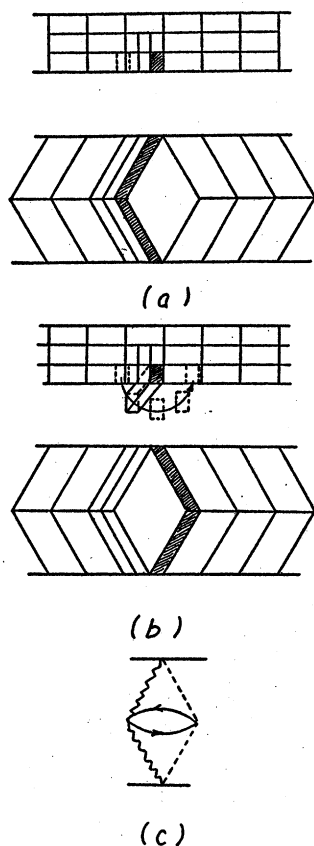| Sample	T°C	Triplet frequencies (±3 cps)			f_2/f_1	f_3/f_1
		f_1	f_2	f_3		
Vinyl stearate A	13.5	420	475	615	$1.13\pm.02$	$1.46\pm.02$
	−1.3	350	405	510	$1.16\pm.02$	$1.46\pm.02$
	−27.8	300	340	435	$1.13\pm.02$	$1.45\pm.03$
Vinyl stearate B	−28.3	200	230	285	$1.15\pm.03$	$1.43\pm.03$
Ethyl stearate	24.0	275	320	420	$1.16\pm.03$	$1.52\pm.03$

(a)

(b)

(c)

Fig. 12. Diagram illus-
trating possible precession
of crystalline domains in
the tilted (β) form of vinyl
stearate.

place at $24.8_5 \pm 0.1_5$°C such that above this temperature
there is no resonance in the region from 50 to 600 cps,
but below the transition the large resonance near 300
cps always appears. A transition between 24 and 25°C
is also indicated by a break in the slope of density-
temperature curves obtained for vinyl stearate. The
appearance and disappearance of the huge resonance
at 300 cps is tentatively ascribed to a transition occuring
in the vinyl stearate while in its β form with the mole-
cules tilted with respect to the planes formed by the
terminal groups. X-ray powder diffraction photographs
show no changes in the long spacing (between planes)
at temperatures from 30 to 0°C so the transition must
involve changes in cross-sectional packing of the chains
or a change from a monoclinic to triclinic unit cell
rather than any change in the angle of the tilt.

At lower temperatures the large resonance in vinyl
stearate splits into a triplet; although the principal
resonance frequency f_1 varies somewhat with tempera-
ture and for different samples, the ratios of the sub-
sidiary triplet frequencies to f_1 is always constant.

The details of the crystalline modification occurring
between 24 and 25°C in vinyl stearate are not as yet
sufficiently clear to define a specific mechanism for the
resonance phenomena, but the results prove conclu-
sively that the dispersions are intimately connected with
the crystalline state of the material. Future measure-
ments are planned on other long chain hydrocarbons
where transitions of a known character occur.

In the meantime one can speculate that a kind of
mechanical spectroscopy eventually may be evolved
yielding information on the actual crystalline state
of solids in much the same way that electromagnetic
spectra aid in determinations of molecular and atomic
structure.

VII. CONCLUSIONS

Complex shear compliance measurements on vinyl
and ethyl stearate yield results depending critically on
the particular crystalline modification in which these
materials exist at the time of measurement. When first
cooled from the melt the materials are in a metastable
form and only a few very small resonance dispersions
are noted in the range 50 to 5000 cps. At later times
numerous large resonances appear; the largest is in the
vicinity of 300 cps for both vinyl and ethyl stearate.

While the vinyl stearate is in a metastable state (for
approximately 60 days) a reversible transition takes